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Kinetics and Mechanism of Fixation of Cu-Cr-As Wood Preservatives*)

Part II. Fixation of Boliden K33

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Kinetics and Mechanism of Fixation of Cu-Cr-As Wood Preservatives
Part II. Fixation of Boliden K33

Summary

After an initial instant ion-exchange fixation of copper and a temporary storage by adsorption of chromic acid, the subsequent precipitation fixation occurs in regions with different chrome fixation rates. The chrome fixation rates are bimolecular in regard to chromic acid. A hypothesis of the mechanism of fixation is given. First acid copper and chrome (III) arsenates are precipitated simultaneously with chromic chromate complex fixation to the wood substance. This is followed by precipitation of tertiary arsenates and basic copper arsenate. Finally basic chromic chromates form. The acid and tertiary copper arsenates and the chromates are intermediates, which after the main reaction period are converted into stable compounds.

Kinetik und Mechanismus der Fixierung von Cu-Cr-As Holzimprägniermittel
II. Die Fixierung von Boliden K33

Zusammenfassung

Nach der anfänglichen unmittelbaren Ionen-Austausch-Fixierung von Kupfer und einer zeitweiligen Adsorption von Chromsäure folgt die Ausfällungs-Fixierung in Regionen mit verschiedener Geschwindigkeit der Fixierung von Chrom. Die Geschwindigkeit der Chromfixierung ist bimolekular hinsichtlich Chromsäure. Eine Hypothese über den Mechanismus der Fixierung wird aufgestellt. Zuerst fallen saure Kupfer und Chrom(III)-Arsenate aus und gleichzeitig fixiert sich ein Chrom(III)-Chromat-Komplex am Holz. Danach fallen tertiäre Arsenate und basisches Kupferarsenat aus. Schließlich bildet sich basisches Chrom(III)-Chromat. Das saure und das tertiäre Kupferarsenat sowie die Chromate sind Zwischenprodukte, die sich nach der Hauptreaktionsperiode in stabile Verbindungen umlagern.

1. Introduction

In Part I of this investigation (Dahlgren and Hartford 1972) was shown that wood affects the pH behaviour of CCA preservative solutions considerably. Ion-exchange reactions and temporary adsorption of chromic acid occur, increasing the pH. The conditions for fixation of the preservative components by precipitation reactions were thereby influenced to a substantial degree, compared to conditions in pure solution systems. General aspects were also given on kinetics, and a number of factors, which might be involved in the fixation process, were discussed.

The kinetics of fixation is in this part experimentally studied on a commercial CCA preservative, Boliden

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Table 1

Kinetic Data for Chrome Fixation in Pine and Spruce Treated with Boliden K33

Species	Solution strength % Boliden K33	Temp. °C	a	Region						At the end of the 2nd region		
				2nd			3rd			Fixation time, hours	Degree of Cr fixation, %	pH
				x_{o2}	$k_2^1)$	$k_2^2)$	x_{o3}	$k_3^1)$	$k_3^2)$			
pine	2	5	0.37	0.02	0.32	1.67	0.04	0.12	0.60	1	15	—
		20		—	—	—	0.03	0.46	2.39	—	—	~3.0
		30		—	—	—	0.03	1.08	5.61	—	—	—
	4	5	0.74	0.07	0.11	0.55	0.25	0.055	0.28	9	46	—
		20		0.05	0.43	2.24	0.13	0.29	1.52	1½	32	2.85
		30		0.05	0.70	3.64	0.27	0.46	2.40	3	61	—
spruce	2	5	0.37	0.02	0.32	1.67	0.07	0.13	0.67	2	26	—
		20		0.04	0.66	3.43	0.08	0.36	1.85	1½	32	3.2
		30		0.03	1.40	7.28	0.07	0.81	4.21	1	31	—
	4	5	0.72	0.06	0.17	0.90	0.25	0.074	0.39	8	50	—
		20		0.07	0.47	2.44	0.18	0.28	1.48	2	42	2.9
		30		0.04	0.94	4.90	0.17	0.59	3.05	1	42	—

a   = chrome content after completion of the main reaction period, in % of weight of dry wood
x_0 = chrome conc. extrapolated to zero time, in % of weight of dry wood
k   = rate constant
1) k^{-1} = chrome conc. in % of weight of dry wood · hour
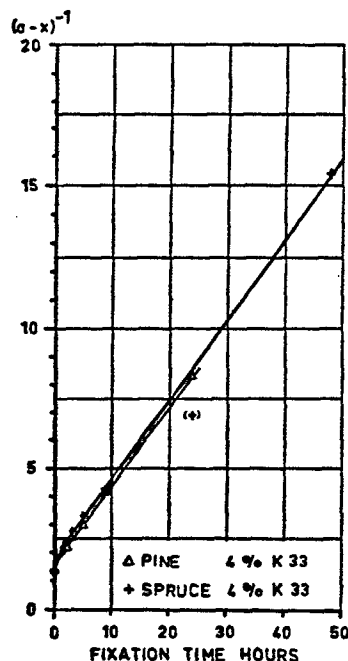2) $k^{-1} = \dfrac{\text{mole Cr} \cdot \text{h}}{\text{kg dry wood}}$
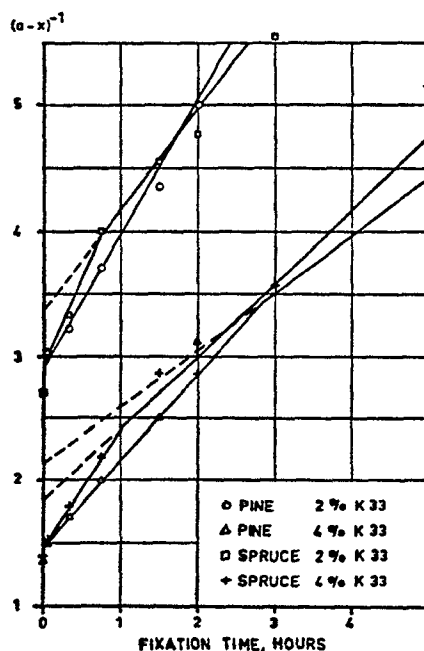

Fig. 4. Chrome fixation of Boliden K33 at 20°C
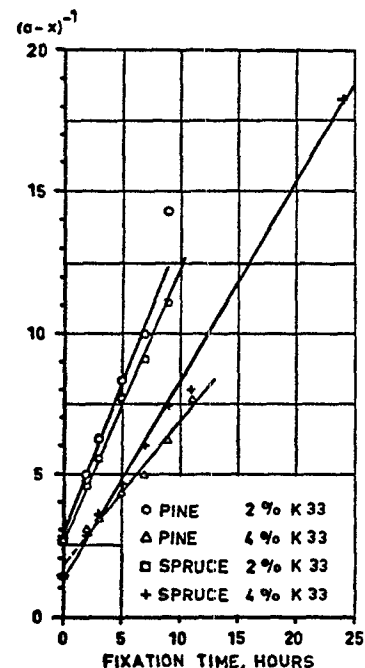

Fig. 5. Chrome fixation of Boliden K33 at 30°C

Fig. 6. Chrome fixation of Boliden K33 at 30°C

approaches completion, the experimental values of $(a - x)^{-1}$ become rather uncertain (a small difference between two large numbers each with a certain inaccuracy). Those data are therefore not used in the figures. To facilitate evaluation the early stages of the course of fixation are shown separately in a larger scale. From the figures the rate constants and axial intersections at zero time have been evaluated, and are given in Table 1. The values of "a" deviate somewhat

from that calculated from a solution with nominal composition.

Two regions with different chrome fixation rates have been established. For reasons given above it has not been possible to decide whether further regions exist later in the course of fixation. As will be seen in Part III an additional rate region can exist at the beginning. In the case of Boliden K33 this region either does not appear or is of so short duration and
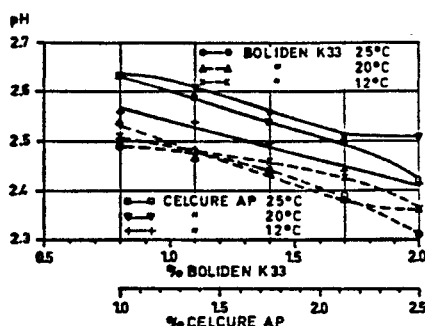
Fig. 8. pH for first appearance of green precipitate in reduced Boliden K33 and Celcure AP solutions
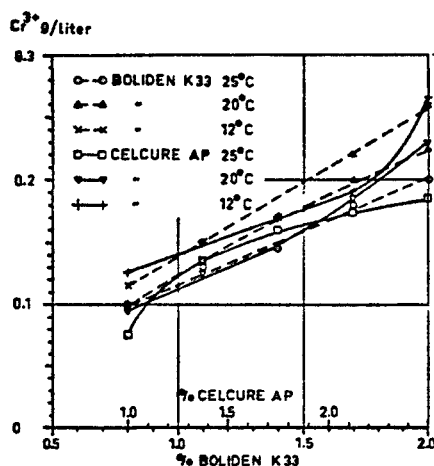

Fig. 9. Content of trivalent chrome for first appearance of green precipitate in reduced Boliden K33 and Celcure AP solutions

At plant conditions the pH of a working solution can occasionally be higher than the limit value for precipitation. Up to a certain point this does not cause trouble in the treatment. A limited amount of sludge can be accepted, which is determined by the pH and by the renewal of the solution. The more frequent the renewal the higher pH can be accepted, because formation of the precipitate takes a certain time. There are indications from sap displacement that the tolerance limit of pH is about 3.0 or slightly lower. On the basis of theoretical calculations Hartford (1970) has suggested an upper limit of about 15% for chrome reduction. This is in good accord with the observed values.

Also not directly applicable to working conditions the precipitation limit conditions give a necessary background to the solution stability problem. They are of direct interest for sampling and analysis. When taking a solution sample at a treating plant, one is interested to know its composition at the time of sampling. In many cases this solution is supersaturated. To avoid precipitation on the walls of the flask the filtered sample should be acidified by one drop of nitric acid per 50 cc sample in connection to the sampling. To dissolve already formed precipitate needs considerably more acid.

When analysing a clear supersaturated CCA solution by X-ray the radiation initiates instant precipitation on the mylar film. The filter action of almost non-visible amounts of precipitate on the film causes serious analytical errors. The remedy is nitric acid addition as indicated above.

5.4 Composition of primarily formed precipitate in reduced CCA solutions

With a slight over-dosage of hydrogen peroxide and a sufficient large solution volume enough precipitate was obtained for analysis. The precipitate was vacuum filtered, washed by water until uncolored filtrate was obtained, sucked dry and dried at room temperature. Copper, chrome and arsenic were determined according to Williams (1970).

The molar composition of the precipitates from the solutions with the lowest and the highest concentrations at the three temperatures studied is given in Table 2. Only traces of hexavalent chrome were found, being neglected. The acidity of the precipitates was calculated by difference (any remaining sodium in the Celcure AP precipitates was not determined and is included in the H:As mole ratio). The temperature has a considerable influence on the acidity represented by the H:As ratio. The minimum acidity was obtained at 20°C for 1.0 and 2.5% Celcure AP and 0.8% Boliden K33 and at 25°C for 2.0% Boliden K33 solutions. With the variations in composition of the precipitates at changed concentration and temperature it is understandable that the precipitation limit conditions are of a complex nature.

Table 2

Composition of primarily formed precipitate at reduction of CCA preservative solutions by hydrogen peroxide

Preservative	Conc. %	Temp. °C	Mole ratios		
			H:As by difference	Cu:As	Cr:As
Boliden K33	0.8	12	0.69	0.06	0.73
		20	0.15	0.06	0.91
		25	0.36	0.09	0.82
	2.0	12	0.52	0.07	0.78
		20	0.69	0.09	0.71
		25	0.29	0.11	0.83
			0.30	0.12	0.82
Celcure AP	1.0	12	0.38	0.08	0.82
		20	0.08	0.05	0.94
		25	0.45	0.06	0.81
	2.5	12	0.55	0.07	0.77
		20	0.28	0.07	0.86
		25	0.58	0.13	0.72

5.5 Simulation of the primary precipitation in presence of wood

After the initial ion-exchange and adsorption reactions between a CCA preservative solution and wood the pH is higher than at the precipitation limits studied in section 5.3. This pH change is simulated by partial neutralisation with sodium hydroxide. The effect of changes in concentration of other ions is considered. The critical chrome reduction was determined at different neutralisation levels with the same technique as before on a 2% Boliden K33 solution. The results are given in Figure 10 and Table 3. The observations are explained in the following way.

6.2 The initial fixation

The initial fixation by ion-exchange reactions occurs so fast that it can be considered as instantaneous. Table 4 gives the fixed amounts of Cu, Cr and As, when extrapolated to zero time. The As content indicates that because of imperfections in the experimental technique some precipitation fixation is included in these results.

Table 4
Initial fixation

$K33$ conc. %	Species	Temp. °C	Extrapolation to zero time		
			% Cu	% Cr	% As
2	pine	5	0.09	0.02	0.01
		20	0.10	0.03	0.01
		30	0.10	0.03	0.02
	spruce	5	0.10	0.02	0.01
		20	0.10	0.04	0.01
		30	0.10	0.03	0.02
4	pine	5	0.11	0.07	0.03
		20	0.12	0.05	0.05
		30	0.11	0.05	0.05
	spruce	5	0.11	0.06	0.04
		20	0.12	0.07	0.06
		30	0.11	0.04	0.05

The pine contained 0.0086 % cold water extractable N calculated on oven dry wood basis and the spruce 0.0072 %. Only 0.0024 and 0.0006 % N respectively occurred as amino acids. The difference was probably inorganic nutrient salts. This shows that the free amino acids cannot explain any initial chrome fixation.

Sawdust was treated with chromic sulfate (1 g Cr/l) and copper sulfate solutions with the same copper contents as 2 and 4 % Boliden K33 solutions acidified with sulfuric acid to the same pH as preservative solutions. The copper fixation was almost identical with the results in Table 4 and the chrome fixation 0.015 %. With solution containing both copper and chromic sulfate the chrome fixation was less. The buffer capacity of these solutions was considerably less than for preservative solutions. This gives an indication but cannot be taken as a proof of the extent of ion-exchange fixation. The ion-exchange fixation may be a chelating mechanism.

If we assume all Cu in Table 4 and 0.01 % Cr to be ion-exchange fixed the mole ratio of the remaining Cr and As is slightly above 1. From the results in section 4 a slightly acid arsenate would be expected to initially precipitate. Considering analytical errors, that some hexavalent chrome might be present (cf. section 6.3) and that during the washing minute quantities of copper arsenates because of incongruent solubility could have been converted into basic arsenates and some initially precipitated As has been removed, the assumption seems to be close to reality. A minor part of the copper is, however, present as arsenate.

The ion-exchange fixation of trivalent chrome is so small that it, except for the initial fixation, can be neglected. The initial precipitation fixation is principally through rapid reduction of chromic acid by small amounts of soluble active reducing agents. Almost identical results with Table 4 were obtained with Boliden K33 solution from oscillating pressure treatment, where about 5 % of the chrome content was trivalent.

In sufficient acid solutions chromic dichromate anionic species are expected to occur (Hartford 1942; Costa 1950; Kasper 1932). Another complex chromate Cr $[(CrO_4)_3]$ exists in solution at pH 2.8 (Chaudbury 1941). This latter one could possibly occur in solution at the early fixation stages. Presence of any low-molecular weight chelating agents emanating from the wood will lead to soluble Cr (III) and cannot explain any fixation.

6.3 The 1st and 2nd precipitation fixation regions

The wood substance is first attacked by the chromic acid at a high rate (easily attacked wood constituents, 1st region) and then at a slower rate (less easily attacked wood constituents or intermediate oxidation products). In several cases the first type of attack is of so short duration and such a small extent that it is not detected.

The assumption that no hexavalent chrome is fixed at the 1st and 2nd region leads in most cases to considerably more than 3 equivalents Cu + Cr (III) precipitated per mole As, which conflicts with the results in the sections 5.5 and 6.4.

Further it was found in section 5.5 that no hexavalent chrome was included in the primary precipitation. With chromotropic acid it was stated that hexavalent chrome was fixed at the end of the 2nd region. This fixation therefore must occur to the wood substance. It is reason to believe that the hexavalent chrome is fixed as the $[Cr(CrO_4)_3]^{3-}$ complex to the wood as this ionic species exists at the actual pH range and as presence of trivalent chrome seems to be necessary for hexavalent chrome fixation. The assumption is further supported by Flomina (1969), who found that Cr^{3+} formed mixed salts with acidic groups of wood and CrO_4.

We assume the mechanism of chromic acid reduction by the wood substance and the reduction reaction rate constant to be the same in the 2nd and the 3rd regions. The higher chrome fixation rate in the 2nd region depends on fixation of hexavalent as well as trivalent chrome, while in the 3rd region there is no hexavalent chrome fixation. Within the 1st region the precipitate has a composition corresponding to acid copper — chrome arsenates. This is also the case in the 2nd region, but in the less acid later stage of it the composition could, depending on the acutal reaction medium, change over to tertiary arsenates. In some cases the change-over to tertiary arsenates may occur within the 3rd region or at the region boundary. The precipitated copper arsenates and the fixed hexavalent chrome are not stable at later stages of the fixation course. After the main reaction period slow conversions take place. This will be discussed later.

The ratio of trivalent to total chrome fixed within the 2nd region is obtained in the following way. At the beginning and at the end of the 2nd region $(a—x_1)^{-1} = f_1$ and $(a—x_2)^{-1} = f_2$, resp. If a straight line is drawn through the intersection between the lines for the 1st and 2nd regions parallel with the line of the 3rd region, the ordinate value of this line at the end of the 2nd region is $(a—x_3)^{-1} = f_3$. The rate constants for the 2nd and the 3rd region are k_2 and k_3, resp. and $x_3—x_1 = \Delta Cr(III)$ and $x_2—x_1 = \Delta Cr_{total}$.

$$Thus = \frac{k_3}{k_2} = \frac{f_3 - f_1}{f_2 - f_1} = \frac{\Delta Cr(III) \cdot f_3}{\Delta Cr_{total} \cdot f_2}$$

For Boliden K33 no 1st region was detected. In this case therefore $x_1 = x_{02}$ in Table 1. Calculated stoichiometric data at the 2nd region for Boliden K33 are given in Table 5. We observe that the lower the temperature, the more hexavalent chrome is fixed in relation to the arsenate fixation and the more are acid arsenates formed instead of tertiary arsenates. The higher the Boliden K33 concentration is, the more chrome is fixed in hexavalent form.

Elution of ion-exchange fixed copper is induced in one case. Although the stoichiometric calculations leed to chemically acceptable results, the description of the mechanism must be taken as a hypothesis, not as a proof. In the case of treatment with 2 % Boliden K33
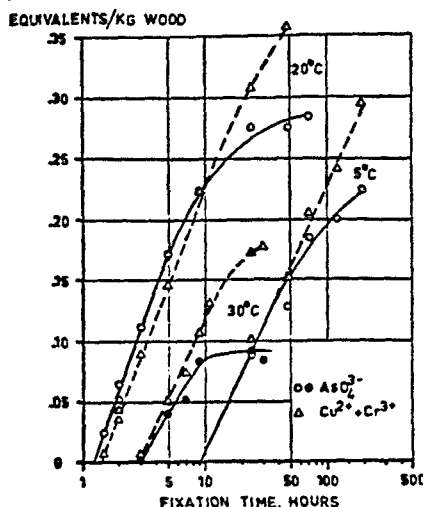
Fig. 13. 3rd region fixation of 4% Boliden
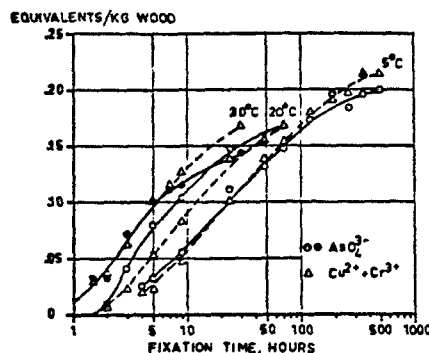K33 solution in pine

Fig. 14. 3rd region fixation of 2% Boliden
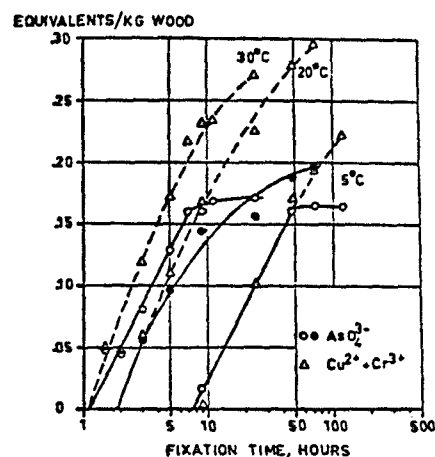K33 solution in spruce

Fig. 15. 3rd region fixation of 4% Boliden
K33 solution in spruce

differs considerably from earlier investigations using indirect experimental technique (e. g. Eadie and Wallace 1962). Some further details not observed with Boliden K33 will be experimentally dealt with in Part III, where the fixation of another, considerably slower reacting CCA preservative is analyzed. There also the final reactions after the main fixation period will be discussed.

Acknowledgement

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Appendix

Direct colorimetric determination of Cr(III) in CCA preservative solutions

Measuring the green color of trivalent chrome in a preservative solution its content is determined. EEL colorimeter model A with filter 606 was used. With this filter chromate does not interfere, but a small correction has to be made for copper.

Standard solution

Dissolve 9.60 g chromic potassium sulfate AR $Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$ in about 200 cc dist. water, heat the solution to boiling, cool and dilute to the mark in a 500 cc volumetric flask. The solution contains 2 mg Cr(III) per cc.

Calibration

Add to a series of dry, clean test tubes 0, 1, 2, 3, 4 and 5 cc of the standard solution and from a burette dist. water to 10.0 cc total volume. Mix well, transfer to a colorimeter tube and take colorimeter readings with water as a reference. Plot readings versus Cr(III) content on a graph.

The copper correction is proportional to the copper concentration in the sample. The copper correction factor is determined by taking a colorimeter reading of a fresh preservative solution of known composition and strength, which is free from Cr(III).

Procedure

Adjust the colorimeter reading to zero against water. Pour the clear sample solution into a colorimeter tube and take the reading. This reading is too high. Knowing the copper concentration in the sample and multiplying it with the copper correction factor, a correction is made. Using the corrected reading the Cr(III) concentration is obtained from the graph. In many cases a satisfactory estimate of the copper content for the purpose is obtained from hydrometer readings if not known otherwise.

Kinetics and Mechanism of Fixation of Cu-Cr-As Wood Preservatives[*)]

Part III. Fixation of Tanalith C and Comparison of Different Preservatives

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Keywords

Kinetics
Fixation
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Picea abies
Pinus sylvestris
Fagus sylvatica
Sarcocephalus diderichii

Kinetics and Mechanism of Fixation of Cu-Cr-As Wood Preservatives
Pt. III. Fixation of Tanalith C and Comparison of Different Preservatives

Summary

The rate of fixation of Tanalith C is, depending on temperature, 5 to 9 times slower than that of Boliden K 33. This enables experimental study of some further details about the mechanism of fixation. The pH characteristic of a preservative seems to be a predominant rate controlling factor of chrome fixation. Addition of sodium sulfate, manganese sulfate or boric acid reduced that rate of fixation. After all chrome has been precipitated slow final reactions occur, converting some earlier precipitated compounds into those stable at final conditions. Final equilibrium fixation products are ion-exchange fixed Cu to the wood, $CrAsO_4$, $Cu(OH)CuAsO_4$ and $Cr(OH)_3$, although highly basic chromic chromates persist for a long time.

Schlüsselwörter
(Sachgebiete)

Kinetik
Fixierung
KCA Imprägniermittel

Kinetik und Mechanismus der Fixierung von Cu-Cr-As Holzimprägniermittel
III. Fixierung von Tanalith C und Vergleich verschiedener Imprägniermittel

Zusammenfassung

Die Geschwindigkeit der Fixierung von Tanalith C ist, abhängig von der Temperatur, 5—9 mal langsamer als die von Boliden K 33. Dadurch werden weitere experimentelle Untersuchungen über Einzelheiten des Fixierungsmechanismus möglich. Der pH-Wert eines Imprägniermittels scheint ein vorherrschender Faktor zu sein, der die Geschwindigkeit der Chrom-Fixierung bestimmt. Zusätze von Natriumsulfat, Mangansulfat oder Borsäure verringern die Fixierungsgeschwindigkeit. Nach Ausfällung der gesamten Chrommenge finden langsame Reaktionen statt, wobei sich einige der primären Ausfällungen in stabile End-Verbindungen umlagern. Die endgültige Fixierung im Gleichgewichtszustand ist eine Ionen-Austausch-Fixierung von Kupfer zu Holz, $CrAsO_4$, $Cu(OH)CuAsO_4$ und $Cr(OH)_3$, obwohl hochbasische Chrom(III)-Chromate über eine längere Zeitdauer bestehen bleiben.

1. Introduction

The hypothesis of mechanism of fixation given in Part II of this investigation (Dahlgren and Hartford 1972), which was tested on Boliden K 33, is now further tested on a different type of commercial CCA preservative, Tanalith C. Evaluation is made from the data obtained by Wilson (1969, 1971). He studied the fixation of Tanalith C in Finnish redwood sapwood (*Pinus sylvestris*), UK grown spruce sapwood (*Picea abies*), UK grown beech sapwood (*Fagus sylvatica*) and opepe heartwood (*Sarcocephalus diderichii*). No mathematical treatment was done on the data obtained.

The rate of fixation of different CCA preservatives are compared and the effect of some additions on the rate is studied.

2. Fixation of Tanalith C

The data obtained by Wilson (1969, 1971) were expressed in per cent of complete fixation as a function of time. Knowing the composition of Tanalith C, the data were recalculated into per cent by weight of wood and kinetic curves plotted for chrome fixation applying the equation

$$kt = (a - x)^{-1} - (a - x_0)^{-1}$$
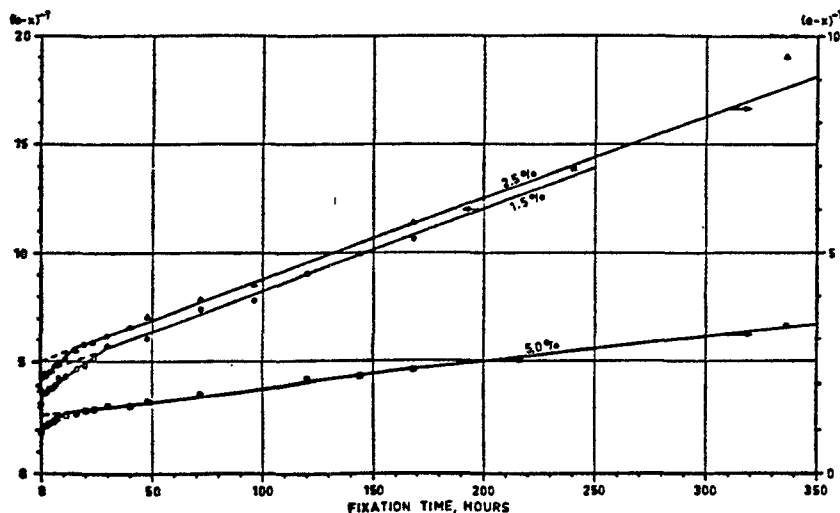
Fig. 1. Chrome fixation of Tanalith C in Finnish redwood at 5°C. a and x = Cr content in % of weight of dry wood
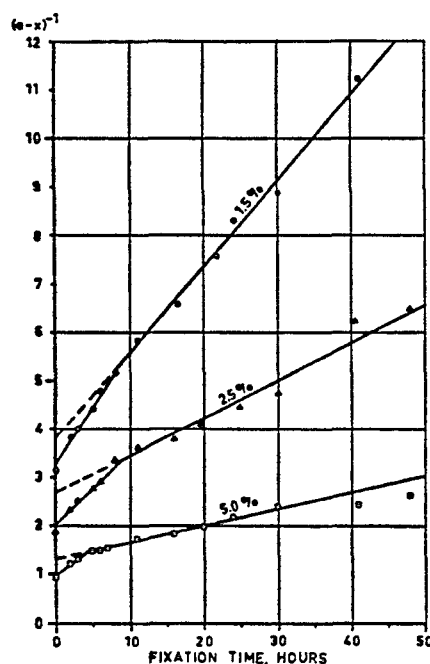
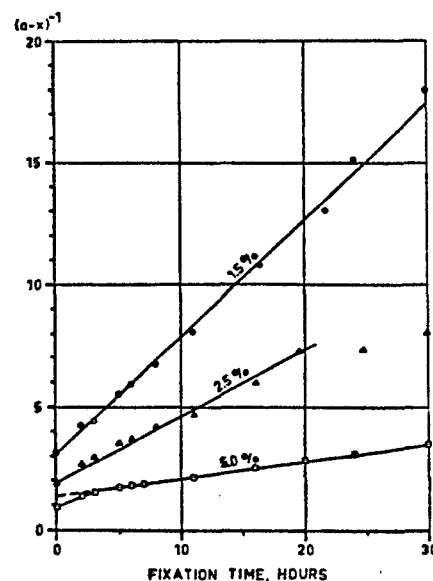Fig. 5. Chrome fixation of Tanalith C in UK grown spruce at 20°C

Fig. 6. Chrome fixation of Tanalith C in UK grown spruce at 30°C
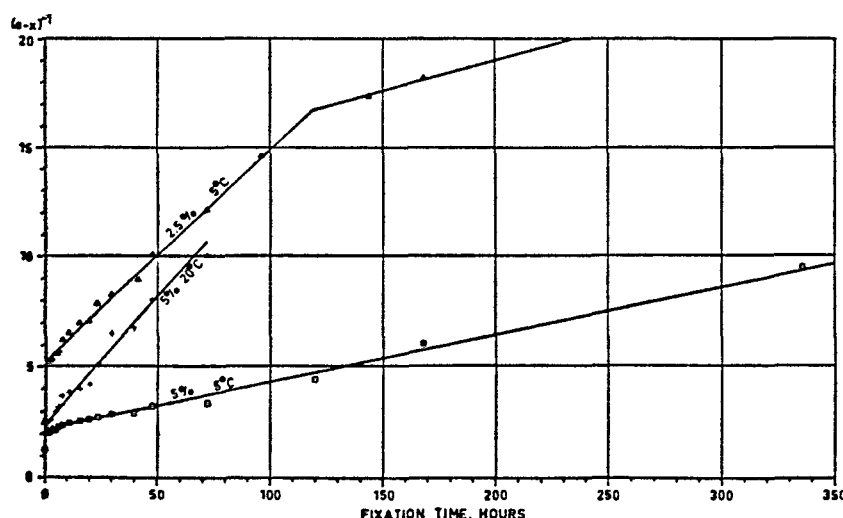
Fig. 7. Chrome fixation of Tanalith C in UK grown beech

factor "B" in eq. 4, Part I, depends mainly on the Cr (VI) concentration at zero time. There is reason to believe that "B" differs with wood species of different character. The higher the energy of activation, the greater is the temperature coefficient of the chrome reduction reaction.

One interesting observation is that at the end of the 2nd region the pH is considerably higher for Tanalith C than for Boliden K 33. The large values of x_{02} and x_{03} (in case only the 3rd region was evaluated) demonstrate that data on preceding regions could have been obtained, if the study had covered shorter fixation times than 2 hours.

In some cases, viz. 1.5 and 2.5% Tanalith C at 20° C and 1.5% at 5°C on opepe and 2.5% Tanalith C on redwood at 30°C the last region observed has a higher rate than the preceding one. This is designated as the 4th region. As discussed in section 6.4 in Part II this is explained by precipitation of basic chromic chromates, giving a chrome fixation rate higher than the chrome reduction rate. In some of the cases related above on Tanalith C the precipitation of arsenate is not complete at the begin of the 4th region. The course of fixation takes place at a higher pH level with Tanalith C than with Boliden K 33. It is therefore likely that at a sufficiently high pH at the early part of the 4th region tertiary arsenates and basic chromic chromates precipitate simultaneously.

The rate constants of Tanalith C are considerably higher for the two hardwoods than for the two softwoods, the energy of activation for opepe determined from Figure 14 being

$$E = 85\,000 \pm 1500 \text{ joule per mole Cr (VI).}$$
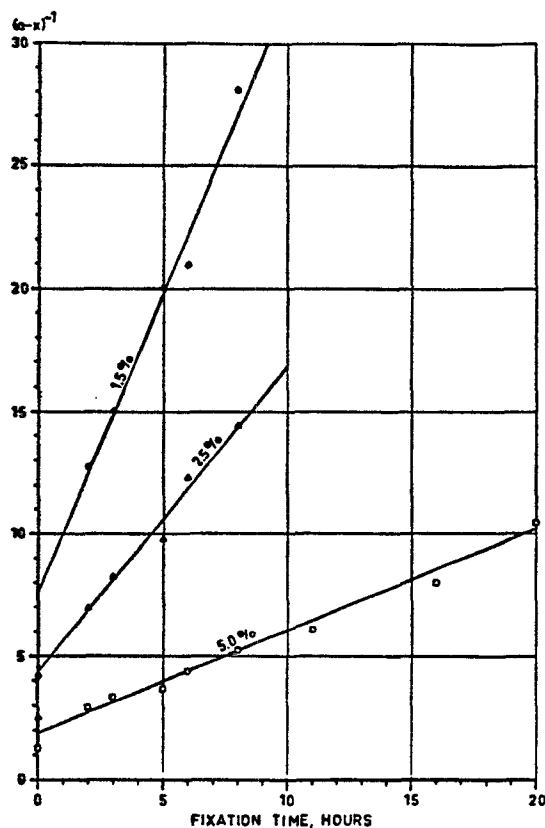
Fig. 12. Chrome fixation of Tanalith C in opepe at 30°C
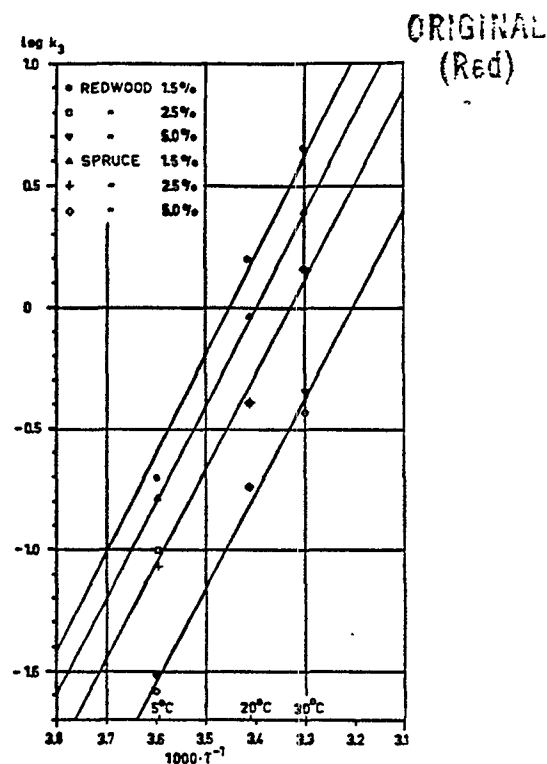
Fig. 13. Arrhenius' equation applied to 3rd region chrome fixation of Tanalith C in redwood and spruce
$k_3 = (\text{moles Cr/kg dry wood})^{-1} \cdot h^{-1}$

Table 1

Kinetic data for chrome fixation in redwood and spruce treated with Tanalith C

Species	Solution strength % Tanalith C	Temp. °C	a	Region						At the end of the 2nd region		
				2nd			3rd			Fixation time, hours	Degree of Cr-fixation, %	pH
				x_{o2}	k_2 1)	k_2 2)	x_{o3}	k_3 1)	k_3 2)			
redwood	1.5	5	0.32	0.04	0.071	0.37	0.10	0.038	0.20	30	45	—
		20		—	—	—	0.04	0.299	1.56	—	--	--
		30		—	—	—	0.18	0.870	4.53	—	--	—
	2.5	5	0.53	0.06	0.045	0.23	0.13	0.019	0.10	15	33	—
		20		0.08	0.155	0.82	0.20	0.077	0.40	10	50	4.0
		30		—	—	—	0.10	0.277	1.44	—	--	—
	5.0	5	1.06	0.11	0.025	0.13	0.31	0.006	0.03	11	33	—
		20		0.04	0.102	0.53	0.37	0.035	0.18	6½	43	3.6
		30		0.00	0.252	1.31	0.36	0.087	0.46	3	45	—
spruce	1.5	5	0.32	0.02	0.045	0.23	0.06	0.031	0.16	23	31	—
		20		0.02	0.242	1.26	0.06	0.176	0.92	8	40	—
		30		—	—	—	0.00	0.478	2.49	—	--	—
	2.5	5	0.53	0.03	0.032	0.16	0.10	0.016	0.083	20	30	—
		20		0.04	0.154	0.80	0.16	0.077	0.40	9	44	4.1
		30		—	—	—	0.01	0.274	1.43	—	--	—
	5.0	5	1.06	0.12	0.017	0.09	0.37	0.0049	0.026	30	41	—
		20		0.03	0.116	0.60	0.30	0.0346	0.180	4½	35	3.6
		30		0.00	0.203	1.06	0.35	0.070	0.364	3	41	—

Note. pH values are obtained from Swedish pine and spruce
a = initial chrome conc. in % of dry weight of wood
x_o = chrome conc. extrapolated to zero time, in % of dry weight of wood
k = rate constant
1) k^{-1} = chrome conc. in % of dry weight of wood · h
2) k^{-1} = mole Cr · h/kg wood

Initial instant reactions	Precipitation fixation, time →					
	Main precipitation fixation period					Final reaction or conversion period
Ion-exchange fixation to saturation of copper Temporary ionexchange takeup of protons and adsorption of chromic acid	Regions of chrome fixation rate					Very slow reactions via dissolution of instable precipitated matter
	1	2	3	4		Proton release reactions: acid and tertiary Cu arsenates → → basic Cu arsenate acid CuCr arsenate →
	1st type Cr(VI) reaction with wood	2nd type Cr(VI) reaction with wood or intermediate oxidation products			$Cr_4(OH)_{10}CrO_4$ and $[Cr(OH)_2]_2CrO_4$	→ tertiary Cr arsenate + basic Cu arsenate
	Release of protons and adsorbed chromic acid from the wood					Proton consuming reactions: chromates → $Cr(OH)_3$
		elution of ion-exchange fixed Cu?				Final equilibrium fixation products: ion-exchange fixed Cu to the wood $CrAsO_4$
	Fixation to wood as $[Cr(CrO_4)_3]^{3-}$					$Cu(OH)CuAsO_4$
		alkali copper chromates?				$Cr(OH)_3$
	$H_mCu_nCr_{\frac{3-2n-m}{3}}AsO_4 \rightarrow CrAsO_4$					
	$H_mCu_{\frac{3-m}{2}}AsO_4 \rightarrow Cu_3(AsO_4)_2$			Cu_2OHAsO_4		
Substantial pH increase	Net continuous pH increase towards a maximum. Proton consumption by chromate reduction dominates					Alternating pH decrease and pH increase until reactions cease

Remarks $k_1 > k_2 > k_3 < k_4$ k = rate constant of Cr fixation, index refers to region

⌐ ¬ = may occur depending on wood species, preservative, concentration and temperature

The composition of the momentary precipitated acid arsenates changes towards tertiary arsenates during the reaction course
Region 1 sometimes does not occur or is of such a small extent and duration, that it cannot be detected
Region 2 finishes, when fixation as chromate to the wood ceases
Region 4 starts, when basic chromic chromates precipitate
pH at region boundaries are different for different preservatives
All Cr is precipitated at the end of the main fixation period

Fig. 15. Schematic diagram of fixation of CCA preservatives

ion-exchange fixation of Cu to the wood
$CrAsO_4$
$Cu(OH)CuAsO_4$ and
$Cr(OH)_3$

A schematic summing-up of the hypothesis and discussions on the course of fixation is given in Figure 15. Assuming equilibrium is reached, the final distribution of the active elements for the actual CCA preservatives is given in Table 3 with none and 25% of the copper fixed by ion-exchange. The chrome excess differs considerably between the preservatives. The chrome excess is one of the factors determining the final pH, which in turn influences on the leachability and availability of the fungicidal and insecticidal compounds.

4. Comparison of the rate of fixation of different preservatives

In section 3 of Part I the possibilities of altering the rate of fixation of a preservative by additions were discussed. The effect on the rate of fixation in pine at 20°C by addition of 0.5% Na_2SO_4, 0.1% $MnSO_4$ and 0.4% boric acid to a 2% Boliden K 33 solution

Table 3

Final equilibrium distribution of active elements of fixed CCA preservatives

Preservative	Distribution in moles per mole As			
	Cu fixed by ion-exchange	Cu_2OHAsO_4	$CrAsO_4$	excess Cr as $Cr(OH)_3$
Boliden K 33	0	0.315	0.685	0.214
	0.157*	0.236	0.764	0.135
Celcure AP	0	0.324	0.676	0.682
	0.162*	0.243	0.757	0.601
Tanalith C	0	0.465	0.535	1.500
	0.233*	0.349	0.651	1.384

* 25% of total copper

has been studied, Figure 16. Surprisingly both $MnSO_4$ and boric acid decreased the rate. Addition of sodium sulfate also had a rate decreasing effect. The reason for the retarding action of alkali sulfate is not clear. Part of this may be an ion-effect. The solubility of most insoluble materials is increased by the presence of a neutral salt, according to the Debye-Hückel theory.

Kinetics and Mechanism of Fixation of Cu-Cr-As
Wood Preservatives*)

IV. Conversion Reactions during Storage

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Keywords
CCA preservatives
Fixation
Conversion reactions

Kinetics and Mechanism of Fixation of Cu-Cr-As Wood Preservatives
IV. Conversion Reactions during Storage

Summary

Precipitates simulating those produced in wood by preservative fixation reactions were prepared by the reduction of Boliden K 33 and Celcure AP solutions with hydrogen peroxide and hydrazine. The pH changes on aging at 20 and 50°C were studied and related to the chemistry of fixation previously described. Hydrolysis of copper arsenates may render arsenic acid temporarily water soluble pending precipitation by trivalent chrome liberated by the slow hydrolysis and reduction by wood of chromic chromates. As the reduction of chrome is the primary driving force for the fixation of Cu-Cr-As preservatives, pH changes were observed in sawdust treated with dilute CrO₃ solutions under different temperature cycles. The pH is essentially independent of temperature during the first three days when chromic chromates are being formed, but the subsequent pH is highly temperature-sensitive. Part of this effect is due to hydrolysis and reduction and part to generation of acidic reaction products in the wood at higher temperatures.

Schlüsselwörter
(Sachgebiete)
KCA Imprägniermittel
Fixierung
Umwandlungsreaktionen

Kinetik und Mechanismus der Fixierung von Cu-Cr-As Holzimprägniermittel
IV. Umwandlungsreaktionen während der Lagerung

Zusammenfassung

Ausfällungen, die bei Fixierungsreaktionen im Holz entstehen, wurden durch Reduktion von Boliden K 33 und Celcure AP-Lösungen mit Wasserstoffperoxid und Hydrazin simuliert. Es wurden die pH-Veränderungen durch Altern bei 20 und 50°C untersucht und mit der früher beschriebenen Chemie der Fixierung in Beziehung gesetzt. Eine Hydrolyse von Kupferarsenaten macht die Arsensäure vorübergehend wasserlöslich, die danach durch dreiwertiges Chrom ausgefällt wird, das sich durch die langsame Hydrolyse und Reduktion von Chromchromaten mit Holz gebildet hat. Da die Reduktion des Chroms die primäre Triebfeder der Fixierung von Cu-Cr-As-Holzschutzmitteln ist, wurden die pH-Veränderungen bei Sägespänen untersucht, die mit verdünnter CrO₃-Lösung in verschiedenen Temperaturzyklen behandelt waren. Während der ersten 3 Tage, wenn die Chromchromate gebildet werden, ist der pH-Wert in der Regel unabhängig von der Temperatur, jedoch danach sehr temperaturabhängig. Der Anlaß hierfür ist sowohl die Hydrolyse und Reduktion als auch die Bildung von sauren Reaktionsprodukten im Holz bei erhöhter Temperatur.

1. Introduction

In the earlier parts of this investigation (Dahlgren and Hartford 1972; Dahlgren 1972) the pH behaviour, the kinetics of chromic acid reduction and the mechanism of chemical reactions at the fixation of different CCA preservatives in wood were studied. It was shown, that we can distinguish between three phases in the course of fixation: initial instant reactions, a main precipitation fixation period and a conversion period, when the primarily formed compounds are converted into compounds stable at the final conditions. The conversion reactions are extended over a substantial period of time, as was seen by pH measurements. It is the aim of this paper to describe more in detail these conversion reactions. In a subsequent paper their effect on some of the properties of the impregnated wood will be dealt with.

2. The conversion reactions

The schematic diagram of fixation of CCA preservatives (Fig. 15 in Pt. III) gives a rough, but incomplete picture of the conversion reactions. To extend the knowledge it was found necessary to form precipitates from CCA solutions in a way simulating as far as possible the conditions in wood. Hydrogen peroxide is

an ideal reduction agent for CCA preservatives as it gives no contamination. The overall reaction is

$$4 H_2AsO_4^- + 8 H_2O_2 + 8 H^+ + 2 Cr_2O_7^{2-} \rightarrow 4 CrAsO_4 + 16 H_2O + 7 O_2$$
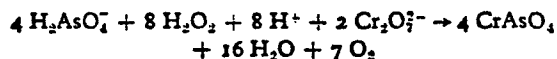
In as much as Cr³⁺ catalyzes the decomposition of peroxide, the amount of peroxide required is always greater than that shown. Its reduction efficiency decreases therefore at increasing chrome reduction. It can be used up to pH 4, but is useless at higher pH. For complete precipitation of a CCA solution thus another reduction agent is needed above pH 4. Hydrazine hydroxide is too alkaline and hydrazine sulfate too acid to simulate the conditions in wood, but a mixture of the two is appropriate. A solution was made containing 40 g hydrazine sulfate per liter to which was added hydrazine hydroxide up to pH 8.0. With this mixture the precipitation in wood could be simulated fairly well. The precipitation of a Boliden K 33 solution was completed at pH 5.0. The reaction in this case is
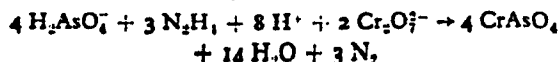
$$4 H_2AsO_4^- + 3 N_2H_4 + 8 H^+ + 2 Cr_2O_7^{2-} \rightarrow 4 CrAsO_4 + 14 H_2O + 3 N_2$$
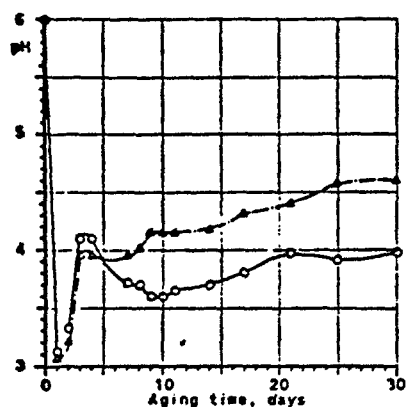
Fig. 2. The pH course during aging of precipitate from Celcure AP

All measurements carried out at 20°C

O = aging temperature 20°C
△ = aging temperature 50°C

With Boliden K 33 at 20°C there is a drop of about 1.4 pH units within 2—3 days, followed by a slow pH increase and steady conditions were reached after about 17 days. At 50°C the pH dropped about 2 units within 1 day followed by alternating pH increases and decreases until after 17 days the pH was almost stable. The final pH is nearly independent of aging temperature.

With Celcure AP the drop in pH is almost 3 units within a day and the 20 and 50°C curves nearly coincide the first 4 days, then diverge and run fairly parallel.

The acidic substances revealed by the pH curves can only exist in appreciable quantity if the proton-consuming reactions are slower than the proton-liberating reactions. This is important and serves to tie the reactions to the experimental curves.

The main difference between the two preservatives is the greater chrome excess in Celcure AP. It is considered that the fresh precipitate of Celcure AP contains a greater fraction of intermediate arsenates than that of Boliden K 33. If so, the rates of proton liberating and proton consuming reactions may soon balance against each other with Boliden K 33 at 20°C, but not at higher temperatures and not with Celcure AP at any temperature, because the conversion of the intermediate arsenates (proton liberating reactions) is speeded up by increase in temperature, while the other reactions do so to a considerably lesser degree.

In a piece of wood the conversion reactions are considerably slower than in a damp filtercake of precipitate used here. This is because the cell walls make the transport of reactants more difficult. Of technical importance is that after the main precipitation fixation period the conversion reactions render part of the primarily fixed arsenate temporarily water-soluble. A leachability test therefore will be considerably affected by how far the secondary fixation of arsenic has proceeded. A greater chrome excess in the preservative formula facilitates the secondary fixation of arsenic.

3. The action of chromic acid on wood at different temperatures

It was believed that the temperature during the course of fixation could have an influence on the pH and the leachability. One possible reason for this

could be, that the reaction products from oxidation of wood substance by hexavalent chrome, and thus their acidity, differ depending on the reaction temperature. Another is the breaking of bonds by hydrolysis of the wood substance at increased temperature liberating acidic groups. It is doubtful that the latter occurs already at 60°C, as in pure water hydrolysis of wood is known to occur at temperatures above 160°C although the reaction is catalyzed by certain multivalent ions.

Experiments were carried out with pine (*Pinus sylvestris*) sapwood sawdust prepared in a cutting mill with a 0.8 mm screen. It was mixed with 0.15% CrO_3 solution in the proportions 8 ml solution to 6 g sawdust on oven-dry basis. The pH was followed during a period of 40 days and the temperature varied from 20 to 60°C in steps of 10°C. In a first series, Figure 3, the temperature was kept constant during the whole period, in a second one, Figure 4, kept at specified temperature the first three days and then stored at 20°C and in a third one, Figure 5, kept at 20°C the first three days and then at the specified temperature. All measurements were carried out at 20°C. For each series a new 20°C trial was made. Differences between the three 20°C curves are due to inhomogeneities in the sawdust and imperfection in the preparation. The key to Figure 3 is valid for the Figures 4 and 5 as well.

In Figure 3 we find that the curves split into two groups 20—40°C and 50—60°C. Within each group the curves have the same character, with slightly lower pH at increasing temperature. At the lower temperatures the pH mainly increases with time with final readings about one pH unit higher than at the start. At the
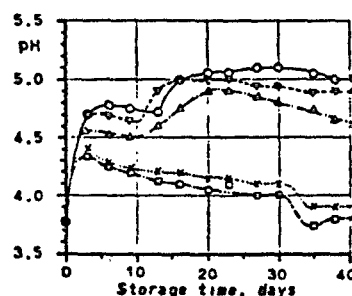

Fig. 3. Chromic acid oxidation of pine sapwood at constant storage temperature. 6 g sawdust (oven dry basis) — 8 ml 0.15% CrO_3 solution. All measurements carried out at 20°C

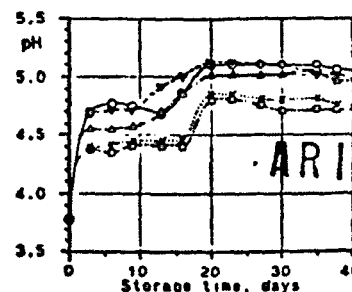|		pH
O = 20°C		
▽ = 30°C	Untreated wood	4.25
△ = 40°C	CrO_3 solution	2.23
X = 50°C	Wood after 3 min	3.78
□ = 60°C		

Fig. 4. Chromic acid oxidation of pine sapwood. Storage at elevated temperatures for 3 days, then at 20°C. Symbols see Figure 3

Kinetics and Mechanism of Fixation of Cu-Cr-As Wood Preservatives

Part V. Effect of Wood Species and Preservative Composition on the Leaching during Storage

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Kinetics and Mechanism of Fixation of Cu-Cr-As Wood Preservatives. V. Effect of Wood Species and Preservative Composition on the Leaching during Storage

Summary

Conversion reactions during storage of CCA treated wood take place even at and below the fiber saturation point as long as ion transport is possible. Increase in drying temperature increases the final pH of the treated wood and the leachability of Cu and decreases slightly the leachability of Cr, while the leachability of As is not affected. This temperature effect is considered to be of no technical importance, but may be of importance when preparing material for biological testing. The length of the wet fixation period before the drying does not influence the results. The presence of alkali sulfates in some preservatives affects the pH of the unleached wood but not the leachability of the active elements. The natural pH of the wood determines to a considerable extent the final pH and the leachability. A correlation was established between the leachability of Cu and As versus the final pH in wood.

When treated with 2—2.5% preservative solutions some wood species: Douglas fir, Ponderosa pine and to a lesser degree Southern yellow pine, showed unexpectedly high As leachability, while on doubling the concentration normal leachability data were obtained. The study included three commercial CCA preservatives: Boliden K33, Celcure AP and Tanalith C, and one experimental variety of Celcure AP without sodium sulfate.

Kinetik und Mechanismus der Fixierung von Cu-Cr-As-Holzschutzmitteln. V. Die Einwirkung der Holzarten und Zusammensetzung der Schutzmittel auf das Auslaugen während der Lagerung

Zusammenfassung

Umwandlungsreaktionen während der Lagerung von KCA-imprägniertem Holz finden bei und unter dem Fasersättigungspunkt statt, solange Ionenbewegung möglich ist. Die Erhöhung der Trocknungstemperatur erhöht den endgütigen pH-Wert des imprägnierten Holzes sowie die Auslaugbarkeit von Kupfer und erniedrigt etwas die Auslaugbarkeit von Chrom, während die Auslaugbarkeit von Arsen unverändert bleibt. Die Einwirkung der Temperatur scheint nicht von technischer Bedeutung zu sein, kann aber beim Herstellen von Material für biologische Prüfung von Bedeutung sein. Die Dauer der Naßfixierung vor der Trocknung beeinflußt die Resultate nicht. Die Anwesenheit von Alkalisulfaten in einigen Schutzmitteln beeinflußt den pH-Wert von unausgelaugtem Holz, jedoch nicht die Auslaugbarkeit der aktiven Elemente. Der natürliche pH-Wert des Holzes bestimmt wesentlich den endgültigen pH-Wert und die Auslaugbarkeit.

Table 2
Changes in relative leaching with time after drying to 22% final moisture ratio

Trial No	Cu	Cr	As	Cu	Cr	As	Cu	Cr	As	Cu	Cr	As	Cu	Cr	As
	0			15			60			120			200		
1	6.4	1.0	10.4	7.0	0.8	10.2	7.0	1.0	10.5	9.1	1.6	11.8	9.9	1.9	12.0
2	2.8	0.5	3.7	4.2	2.0	4.3	4.0	0.9	4.4	5.1	1.3	4.6	5.6	1.3	6.2
3	8.0	0.3	11.5	7.8	0.6	10.1	8.0	1.1	10.1	5.5	0.6	6.9	9.9	1.6	11.2
4	4.4	0.7	4.9	4.7	0.7	4.4	4.7	1.2	4.1	4.2	1.0	3.3	5.3	1.0	4.7
5	10.3	0.5	12.4	11.6	0.8	12.9	9.3	1.6	10.9	12.2	1.0	13.5	12.3	1.0	12.8
6	6.4	0.5	5.0	6.7	0.5	4.4	7.3	1.2	6.0	7.3	1.0	6.5	8.0	0.9	5.4
7	7.8	1.3	10.9	9.9	0.6	12.1	7.6	1.0	10.5	10.1	1.9	10.2	9.5	1.1	10.8
8	3.6	0.8	3.9	6.2	1.4	5.7	4.4	1.3	4.7	5.1	1.4	3.9	6.2	1.1	5.5
9	8.7	0.8	10.8	7.4	0.8	11.9	9.7	0.8	11.0	9.1	1.9	10.8	11.0	1.2	11.3
10	2.2	0.7	4.1	4.2	1.4	5.7	6.0	1.0	5.6	6.0	1.6	5.7	8.9	1.3	6.7
11	10.6	0.8	12.2	11.6	1.0	11.8	12.9	1.1	12.3	8.7	0.8	9.2	14.1	0.4	12.5
12	8.0	0.8	6.3	9.3	1.2	6.6	8.0	1.2	6.3	8.9	0.9	4.6	10.0	1.1	6.1

Table 3
Changes in relative leaching with time after drying to 32% final moisture ratio

Trial No	Cu	Cr	As	Cu	Cr	As	Cu	Cr	As	Cu	Cr	As	Cu	Cr	As
	0			15			60			120			200		
13	7.7	1.4	12.1	7.8	0.8	9.8	9.3	1.0	9.7	6.9	2.6	16.4	13.1	0.3	11.7
14	3.8	1.6	4.5	4.9	1.6	4.4	8.2	2.6	6.5	4.4	0.9	4.4	7.8	0.5	4.1
15	9.0	1.3	11.4	8.9	0.6	10.5	10.8	0.6	10.3	10.4	0.5	10.5	16.5	0.2	9.8
16	4.7	1.0	4.0	5.3	1.0	4.5	6.2	1.0	5.2	7.1	0.8	4.6	7.8	0.2	3.2
17	10.1	1.3	12.6	10.3	0.5	12.7	12.4	1.0	14.2	7.8	0.5	11.2	13.1	0.1	11.5
18	6.9	0.9	5.8	6.9	0.4	6.0	8.0	1.3	11.7	6.7	0.8	6.2	8.7	0.4	5.2
19	7.8	0.6	11.0	8.0	0.5	10.4	9.1	1.4	10.8	9.1	0.8	9.2	10.4	0.3	9.7
20	4.4	0.7	4.1	4.4	0.3	3.9	7.1	1.3	5.6	7.3	0.9	4.1	6.9	0.4	3.5
21	8.2	0.3	11.1	9.9	0.5	11.0	8.9	0.5	10.6	9.9	1.0	11.4	15.6	0.2	11.5
22	6.0	0.8	5.1	6.4	0.5	4.9	6.2	1.0	5.2	7.1	0.9	6.2	11.3	0.7	5.2
23	11.8	1.1	12.2	11.8	0.6	12.2	11.0	1.0	10.9	13.1	1.0	11.7	20.9	0.2	17.0
24	9.6	0.8	10.3	8.7	1.0	6.7	10.8	0.9	6.4	5.8	0.4	5.6	9.1	0.4	4.9

Table 4
Variance analysis of the effect of drying conditions on pH and Cu relative leachability of CCA treated pine sapwood 200 days after drying

Source of variation	Degrees of freedom	pH Mean square	Variance ratio	Significance[1]	Cu Mean square	Variance ratio	Significance[1]
Between levels of factor:							
A, drying temperature	2	0.20366	47.9	***	22.956	7.23	**
B, preservative	1	1.06260	250	***	153.521	48.4	***
C, length of wet fixation	1	0.00844	1.99	o	10.534	3.32	o
D, final moisture ratio	1	0.19984	47.0	***	38.761	12.2	***
Interactions: AB	2	0.00003	o	o	2.128	0.67	o
AC	2	0.00473	1.11	o	7.787	2.45	o
AD	2	0.02267	5.33	**	3.306	1.04	o
BC	1	0.00400	0.94	o	0.260	0.08	o
BD	1	0.00010	o	o	9.753	3.07	o
CD	1	0.00006	o	o	0.093	0.03	o
3- and 4-factor interactions	9	0.00425	—	—	3.175	—	—

[1] *** highly significant, that is $F \geqslant 1\%$ value
** significant, that is $F \geqslant 5\%$ value, but $< 1\%$ value
* possibly significant, that is $F \geqslant 10\%$ value, but $< 5\%$ value
o not significant, that is $F < 10\%$ value

AR100030

The drying rates were chosen so as to correspond roughly to technical conditions at the actual temperatures.

During the drying period the flasks were fitted with covers with a hole to allow a controlled evaporation of water. The drying was checked by weighing each working day. Each time the sawdust was mixed and pressed. If necessary the weight

dependant than at 22%. As could be expected from the chemical composition and the earlier investigations in Pt. I, Celcure AP gives throughout higher pH values than Boliden K33. If we compare with the pH studies on pine without drying in Pt. I, only a slight uniform decrease in pH with time was expected. Note the difference in starting point between Table 1 and in Pt. I. With other wood species the pH behaviour can be different.

3.2 Effect on leachability

The fluctuations with time in Cr leachability are mainly within the limits of the analytical and experimental errors. There are no significant differences in relative Cr leachability between the two preservatives. Storage at 22% final moisture ratio gives a highly significant higher Cr leaching than at 32% moisture ratio. The effect of drying temperature and interaction between preservative and the length of wet fixation are significant. With drying at 20°C to 32% moisture ratio a peak in Cr leachability was observed with both preservatives, but it occurred at an earlier stage with Celcure AP.

There is a general tendency that the Cu leachability fluctuates rather much during drying. With the assumption that the relative leaching, when the reactions have ceased, is proportional to a power of the proton activity we obtain

$$\log y = a - b \cdot x \qquad [Eq. 2]$$

where y = the relative leaching in %
              x = the pH value
              a and b are constants.

Applying this equation to the pH and Cu leachability data after 200 days storage in the tables 1—3, a regression analysis gives
$a = 3.01$ std. error 0.20; $b = 0.48$ std. error 0.05; multiple correlation = 0.907; significance >99%.

The corresponding curve and actual data are plotted in Figure 1. The leachability of Cu is significantly decreasing with increasing pH after 200 days storage. The Cu leachability significantly increases with increasing drying temperature. After 200 days storage the Cu leachability is higher than immediately after drying, as could be expected from the pH data.
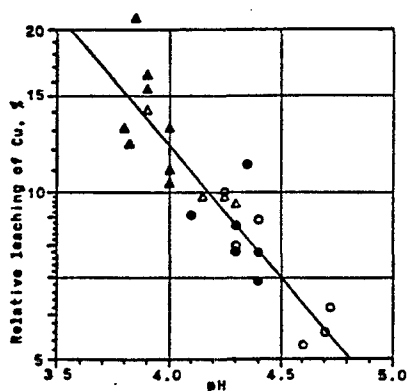
Fig. 1. Relative leaching of Cu in pine sapwood versus pH. 200 days storage at 20°C after drying.

△ Boliden K33, 22% final moisture ratio
▲ Boliden K33, 32% final moisture ratio
○ Celcure AP, 22% final moisture ratio
● Celcure AP, 32% final moisture ratio

With drying at 20°C to 32% moisture ratio a peak in As leachability was observed, which corresponds to the peak in Cr leachability mentioned above. No correlation could be obtained between pH and As leachability. The choice of preservative is the only significant factor. The average relative As leachability is 11.8% for Boliden K33 and 5.1% for Celcure AP. This is explained by the greater chrome excess in the latter case.

3.3 Remarks

The results presented show that conversion reactions can take place at and below the fiber saturation point. How far the moisture ratio can be decreased for this still to occur is not known at present. At 7% moisture ratio no reactions take place. The limit is thus somewhere between 7 and 22% moisture ratio. From a physical point of view conversion reactions are possible as long as the moisture ratio is high enough to allow ion transport. Within a transition range the ion transport is supposed to be gradually rendered more difficult at decreasing moisture ratio. There is reason to believe that the observed higher Cr leachability at 22% final moisture ratio depends on incomplete conversion reactions caused by hindrance of the ion transport below the fiber saturation point.

A decrease in drying temperature gives a decrease in Cu leachability and a minor increase in Cr leachability, while As leachability is not affected. The effects on the leachability of the drying temperature and other process conditions studied are considered in most cases not to be of a magnitude of technical importance. When preparing material for field, green-house and other biological testing the differences can be of a certain importance. In these cases there may be reason to specify the drying conditions to correspond to conditions in practice. A too rapid drying of specimens of small dimensions may inhibit the fixation reactions at too early a stage or render them considerably more difficult. The effect of storage and drying conditions of other wood species on leachability can be different from that of pine.

It is advisable to protect treated timber from rainfall during the main precipitation fixation period. The length of the period is given by the time for the first pH peak when treating sawdust of the actual wood species at actual temperature with actual preservative and preservative concentration. If unprotected a loss of preservative in the surface layer of the timber can occur. In treated timber dried in open air or in driers to a moisture ratio of its final use the lack of completeness of the conversion reactions may in most cases be neglected. As regards leachability open air drying offers some advantage to forced drying. This may be considered for preserved timber subject to severe leaching conditions as in cooling towers and for marine use.

4. Leachability and pH course during fixation of CCA preservatives in different wood species

The pH course during fixation of different CCA preservatives in pine and spruce was described in Pt. I. Using the same technique the study has been extended to cover some other wood species of technical importance from different parts of the world. The pH was followed at 20°C up to 200

Let us now consider the change of pH in wood

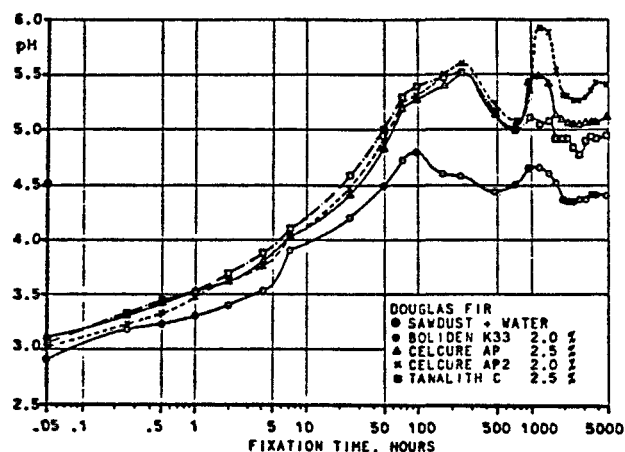$$\Delta pH = pH \text{ (200 days)} - pH \text{ (untreated wood).} \qquad \text{[Eq. 3]}$$

We use the pH data after 200 days wet fixation, 10 days drying and rewetting given in Table 7 and carry out a variance analysis. The results are given in Table 8. All main effects and two-factor interactions are statistically highly significant. The three-factor interaction mean square, which is taken to give an estimate
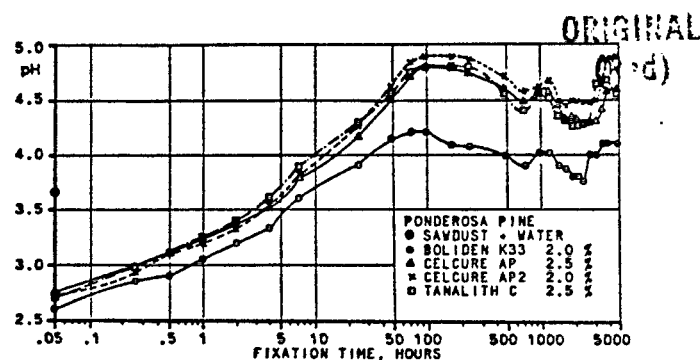

Fig. 7. pH course during fixation at 20°C — Douglas fir

Fig. 8. pH course during fixation at 20°C — Ponderosa pine

Table 7

Sawdust leachability test and pH after wet fixation of different wood species treated with CCA preservatives. In each trial 6 g sawdust on oven dry basis + 8 ml preservative solution

Wood species	pH of wood	Preservative	%	pH after 200 days of wet fixation at 20°C	pH after drying 10 days at room temp. in open air and rewetting to original weight	Relative leaching in %		
						Cu	Cr	As
Pine Sweden	4.10	Boliden K33	2	4.00	4.10	11.2	1.3	15.3
			4	4.15	4.28	8.3	0.9	8.5
		Celcure AP	2.5	4.40	4.53	1.2	0.9	11.2
			5	5.50	5.60	3.2	1.2	4.5
		Celcure AP2	2	4.47	4.62	7.7	1.7	8.6
			4	6.10	6.15	1.2	1.1	4.8
		Tanalith C	2.5	5.25	5.37	5.9	4.0	5.0
			5	6.30	6.35	1.0	0.7	1.8
Spruce Sweden	4.49	Boliden K33	2	4.90	5.00	2.1	0.5	14.1
			4	5.20	5.25	1.8	0.6	12.9
		Celcure AP	2.5	5.30	5.40	8.0	1.4	6.9
			5	6.00	6.10	1.6	0.6	6.9
		Celcure AP2	2	5.65	5.70	1.0	0.5	18.8
			4	6.15	6.23	1.1	0.6	2.4
		Tanalith C	2.5	5.55	5.62	1.3	0.8	2.5
			5	6.20	6.25	0.8	0.3	1.5
Larch Austria	4.32	Boliden K33	2	4.52	4.55	2.9	1.6	10.7
			4	4.65	4.72	1.7	0.8	7.2
		Celcure AP	2.5	5.25	5.30	1.6	1.0	3.0
			5	5.60	5.70	2.0	1.1	2.9
		Celcure AP2	2	5.75	5.82	1.8	1.3	4.1
			4	6.10	6.18	1.5	0.9	3.0
		Tanalith C	2.5	5.12	5.18	4.5	3.2	6.5
			5	5.40	5.42	1.9	0.9	2.3
Beech Sweden	5.57	Boliden K33	2	5.20	5.42	0.6	0.5	10.3
			4	5.20	5.38	0.5	0.2	5.6
		Celcure AP	2.5	6.05	6.20	0.7	0.4	1.1
			5	6.10	6.30	0.7	0.2	0.7
		Celcure AP2	2	6.50	6.55	0.7	0.3	1.0
			4	6.65	6.82	0.3	0.3	0.5
		Tanalith C	2.5	6.42	6.55	0.4	0.2	0.2
			5	6.60	6.80	0.4	0.2	0.2
Radiata pine New Zealand	4.28	Boliden K33	2	4.52	4.45	5.1	1.6	12.0
			4	4.70	4.65		1.1	7.6
		Celcure AP	2.5	5.17	5.17			
			5	5.45	5.45	1.2	0.9	4.4
		Celcure AP2	2	5.45	5.40	2.1	1.3	4.0
			4	5.90	5.98	1.3	0.9	4.4
		Tanalith C	2.5	5.05	5.10	2.2	1.0	2.9
			5	5.48	5.63	1.2	0.5	1.7

to 2 and 4% Boliden K33 solutions, washed and analyzed as described in Pt. II. We find that most of the species fix about 0.10% Cu, beech about 0.20% and eucalyptus and southern yellow pine about 0.13%. Boliden K33 gives throughout the lowest final pH, while the ranking of the others as to the final pH varies with the wood species. On the average the ranking is:

Boliden K33, Celcure AP, Tanalith C and Celcure AP2.

The only difference in composition between Celcure AP and Celcure AP2 is the presence of some sodium sulfate in the former one and its absence in the latter one. To illustrate the effect of the sodium sulfate on the final pH we carry out a variance analysis as above, but consider only these two preservatives. The results are given in Table 11. The three-factor interaction mean square corresponds to a standard error in a single

Table 10
Ion-exchange fixation of copper in different wood species

6 g sawdust on oven dry basis + 8 ml CuSO₄ solution
A = Cu conc. corresponding to a 2% Boliden K33 solution
B = Cu conc. corresponding to a 4% Boliden K33 solution

Wood species	Ion-exchange fixed copper in % of dry wood weight	
	A	B
Pine, Sweden	0.10	0.11
Spruce, Sweden	0.10	0.11
Larch, Austria	0.10	0.10
Beech, Sweden	0.19	0.20
Radiata pine, New Zealand . .	0.11	0.11
Eucalyptus, Corsica	0.13	0.13
Southern yellow pine, USA .	0.13	0.14
Douglas fir, USA	0.09	0.09
Ponderosa pine, USA	0.09	0.09

Table 11
Variance analysis of the difference between Celcure AP and Celcure AP2, that is the effect of sodium sulfate, on change of pH in wood, Eq. 3, by preservative concentration and wood species

Source of variation	Degrees of freedom	ΔpH		
		Mean square	Variance ratio	Significance[1]
Between levels of:				
A, preservative	1	1.2996	72	***
B, concentration	1	1.7601	97	***
C, wood species	8	0.8846	49	***
Interactions AB	1	0.0441	2.44	o
AC	8	0.0140	0.77	o
BC	8	0.1355	7.48	***
Remainder = interaction ABC	8	0.0181	—	

[1]) Legend see Table 4

Table 12
Variance analysis of the effect on the relative leachability by preservative, preservative concentration and wood species

Source of variation	Degrees of freedom	Cu leachability			Cr leachability			As leachability		
		Mean square	Variance ratio	Signif-icance[1]	Mean square	Variance ratio	Signif-icance[1]	Mean square	Variance ratio	Signif-icance[1]
Between levels of:										
A, preservative	3	23.018	9.53	***	0.620	2.43	*	155.407	17.7	***
B, concentration	1	39.161	16.2	***	6.125	24.0	***	566.722	65	***
C, wood species	8	18.409	7.62	***	2.414	9.47	***	92.626	10.6	***
Interactions AB	3	0.758	0.31	o	1.141	4.47	**	11.592	1.32	o
AC	24	4.330	1.79	*	0.215	0.84	o	8.729	1.00	o
BC	8	1.798	0.74	o	0.899	3.53	***	63.317	7.23	***
Remainder = interaction ABC	24	2.416	—		0.255	—		8.763	—	

[1]) Legend see Table 4

Table 13
Variance analysis of the difference between Celcure AP and Celcure AP2, that is the effect of sodium sulfate, on the relative leachability

| Source of variation	Degrees of freedom	Cu leachability			Cr leachability			As leachability		
		Mean square	Variance ratio	Signif-icance[1]	Mean square	Variance ratio	Signif-icance[1]	Mean square	Variance ratio	Signif-icance[1]
Between levels of:										
A, preservative	1	2.151	0.59	o	0.007	0.71	o	4.840	0.57	o
B, concentration	1	11.335	3.10	o	0.563	5.74	**	211.218	25	***
C, wood species	8	4.481	1.23	o	0.780	7.96	***	48.315	1.72	o
Interactions AB	1	0.027	0.01	o	0.022	0.22	o	17.085	1.62	o
AC	8	2.378	0.66	o	0.061	0.62	o	2.326	0.28	o
BC	8	1.195	0.33	o	0.151	1.54	o	31.624	3.74	**
Remainder = interaction ABC	8	3.651	—		0.098	—		8.452	—	

[1]) Legend see Table 4
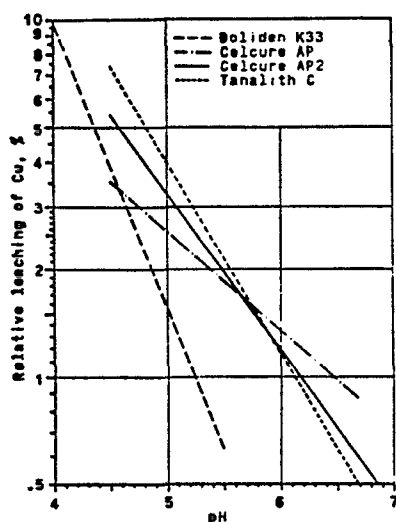
Fig. 9. Relative leaching of Cu according to regression analysis of data in Table 7
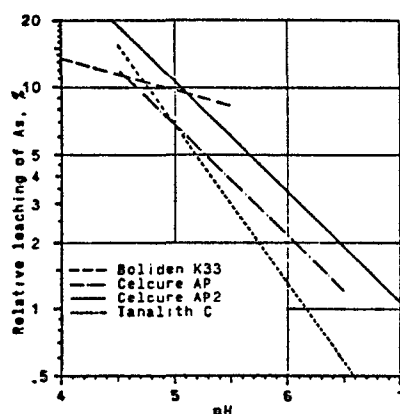

Fig. 10. Relative leaching of As according to regression analysis of data in Table 7

AP2 and Tanalith C, while Boliden K33 gave a lower correlation and a low significance. The regression curves are given in Figure 10. The parallel shift between Celcure AP and Celcure AP2, as a consequence of the sodium sulfate effect on pH, is evident.

4.4 Remarks

The Boliden K33 curve for As leachability has quite a different slope than the curves for the other preservatives although partly within the same area. The dissimilar character of the As leaching curves indicates that there can be a difference between Boliden K33 and the other CCA : s as regards the composition of the arsenic compounds after storage. As Boliden K33 has a lower chrome excess than the others, the conversion of the primarily formed arsenates is less favoured and may be incomplete. If this is true, the arsenates formed with Boliden K33 are the less leachable ones below pH about 4.5, while above this pH value the arsenates formed with the other CCA:s are the less leachable ones. In this context the poor significance of the Boliden K33 curve must be considered.

At the lower concentration level all four preservatives show very high As leachability in Douglas fir and

Ponderosa pine, but at the higher concentration level the As leachability is about the same as for most of the other wood species.

Southern yellow pine shows a similar behaviour although less extreme. Douglas fir data at the lower concentration level fit the As regression curves badly. Here some additional factor must contribute considerably. No explanation can be given at present. Unexpectedly, 2.5% Tanalith C gives the highest As leachability of all CCA:s in Douglas fir. Beech shows the lowest As leachability of all wood species investigated. This is understandable as it has the highest natural pH and thus the highest final of pH all wood species, in spite of its higher ion-exchange fixation of Cu, which decreases the chrome excess. We must here consider the possibility that after the actual fixation time of 200 days, in some wood species the conversion reactions may have virtually ceased and in others not. The anatomy of a wood species may affect the transport of reacting ions at the conversion reactions, rendering it easier in some cases and more difficult in other cases.

5. Comments

The effect of the relative proportions of Cu, Cr and As on their leachability has been studied by a number of authors, e. g. Fahlstrom et al. (1967), Henry and Jeroski (1967), Häger (1969) and Smith and Williams (1973). Indications were given by Häger (1969) that during storage of CCA treated pine slow reactions took place influencing the leachability of the active elements. The present series of investigations is capable of explaining a number of phenomena observed in the papers mentioned above. For future development work it shows the necessity that the conversion reactions taking place during storage must be taken into consideration. The most important factors determining the leachability of CCA treated wood seem to be the concentration and type of preservative, the drying and storage conditions and the choise of wood species. Important wood properties are the ion-exchange fixation capacity of Cu, the natural pH, the chemical composition and the anatomy. Fixation and leachability are indeed of a complex nature. It is the author's expectation that this series of investigations may act as a useful basis for future research on CCA preservatives.

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Dahlgren, S.-E. 1972. The course of fixation of Cu-Cr-As wood preservatives. Record 1972 Annual Conv. Brit. Wood Pres. Ass. 109—128.